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McKenzie, Jack, "A Study of Perovskite-Based Memristors" (2023). *Mechanical Engineering and Materials Science Independent Study*. 240.

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A Study of Perovskite-Based Memristors

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(Dated: August 30, 2023)

Perovskite materials are promising materials that can be used to construct memristors for modern computing applications. Strontium titanate (STO) & Barium Titanate (BTO) are fabricated and measured to see if they were promising material for us. Measurements of the devices are discussed.

I. INTRODUCTION

Memristors are a two-terminal electrical component that are crucial to the future of electronics. The name coming from "memory" and "resistor", the memristor relates the flux and charge of a device. It acts like a malleable water pipe in the sense that when the water stops flowing, the pipe remains in the stretched position, remembering the amount that passed. The memristor, in this sense, remembers the amount of charge that passes through the device. With new technology continuing to grow and the rise of Artificial Intelligence reaching new heights, Moore's law is starting to slow down as creating smaller transistors while still being able to double them has become a challenge. In-memory technology using memristors is a promising approach to address the challenges posed by this slow departure from Moore's Law. Memristors for in-memory computing allow us to solve several bottlenecks of modern computing such as reducing data movement, enabling a higher memory density, and boosting energy efficiency [1].

The data movement between memory and processing units is one of the major bottlenecks of modern computing. Memristors in in-memory computing will enable computation in the location that the data is stored, thus reducing the need to transfer large amounts of data between other units that are separate. A higher memory density is achieved in the fact that memristors can be densely packed into smaller spaces. This will allow for more higher memory capacities while still being able to have a smaller physical space. This is important for dynamic random-access memory (DRAM) in devices, as DRAM is one of the main devices that are starting to face limitations due to the amount of transistors needed to be inserted into the device. Finally, energy efficiency will be further improved due to the fact that the memristor will retain data while in the off state. This will boost energy efficiency a significant amount and help with the machines data persistence in applications such as artificial intelligence [2].

Therefore it is imperative to realize a memristor device that could be used in modern electronic devices. Commercial fabrication of memristors is still being researched as the scalability and reliability of memristor devices are not at the requisite standard. The key to understanding the memristor functionality is to learn the two main mechanisms that govern its attributes, the ionic mechanism and vacancy mechanism. The ionic mechanism involves the movement of ions within the memristor. Applying a voltage across the memristor causes an electric field that drives the movement of

ions and changes its resistance. Applying a bias in either direction will increase or decrease the memristors resistance depending. The vacancy mechanism involves the use of vacancies in the material. Vacancies being a spot in the lattice of the material where an atom is missing from a place it should be. Similar to the ionic mechanism, when a voltage is applied to the material, the oxygen vacancies are migrated to a side as per the voltage bias. This alters the composition of the material and changes its resistance. Both of the main mechanisms are similar in use but vary in style. They both resolve around the fact of changing the materials resistance. This is important because one of the main factors that is studied to determine if a material functions as a memristor is measuring the current vs voltage. The graph that a memristor should exhibit looks like a pinched hysteresis loop (Refer to 1)[3]. The hysteresis referring to the fact that the return path is not similar to the initial path in the memristors behavior. This shows that the memristors resistance depends on its past history, which confirms its importance for future works in memory and modern computing.

The typical memristors that are created are made using metal oxide materials (typically transition metal oxides) such as titanium dioxide (TiO_2) or hafnium oxide (HfO_2). We did fabricate a TiO_2 device, but our main focus on the research was realizing a reliable memristor device based off of perovskite. Perovskite materials are a class of compound that follow the formula ABX_3 , and consist of a three-dimensional network of corner-sharing BX_6 octahedra. "A" can be occupied by various elements such as metals, non-metals, and organic cations. "B" for the formula refers to a metal cation such as titanium, strontium, or lead. "X" for the formula refers oxygen anions. "B" in the octahedra refers to the central atom or ion, and the "X" refers to the surrounding atoms or ions. The 6 indicates that there are six surrounding X ions forming an octahedral shape around the central B ion. The perovskite materials of choice were Barium Titanate (BTO) & Strontium Titanate (STO). BTO & STO are promising perovskite materials for future memristor applications. BTO & STO were used as the active layer material in the memristor for several reasons. 1) They are non-volatile, meaning they can retain a polarization state when an electric field is applied and maintain their resistance state even when power is removed. 2) They can exhibit high resistance contrast, meaning they can have very high-resistance and low-resistance states, otherwise referred to a high on/off ratio. 3) They can be tuned through using different doping and growth methods to better adjust their memory ability.

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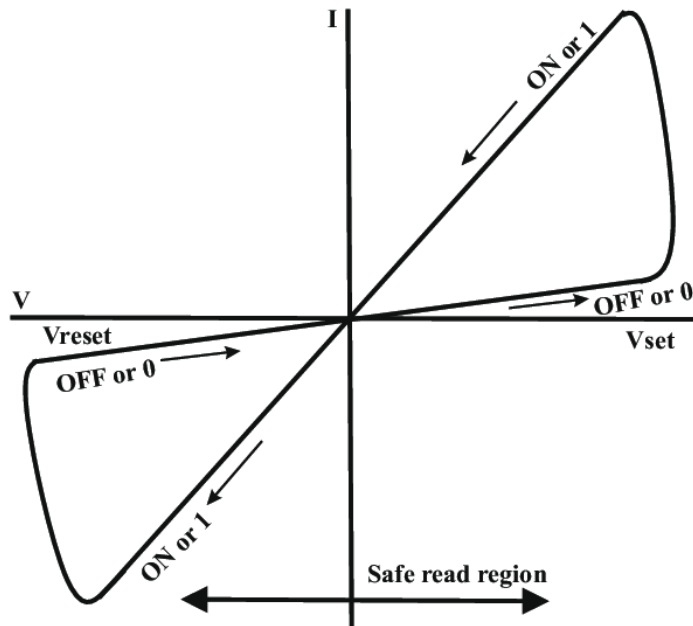


FIG. 1. Memristor current vs voltage graph showing on and off states. (0,0) on the graph represents when the material is in a "reset" state or high-resistance state. The voltage is increased and the current also begins to rise. It starts off looking linear and represents an ohmic behavior. But as it reaches the voltages compliance limit, it undergoes a non-linear transition and moves to a low-resistance state. This is where a sharp curve happens as the current increases significantly with a small change in voltage. It then goes through the opposite, with the voltage being reduced and transitioning back into the high-resistance state.

II. DEVICE FABRICATION

The plan for our memristor was to create a structure of metal/3D material/metal (from bottom to top). The metals act as a top and bottom electrode of the device to allow the memristor mechanisms to function.

II.1. Growing Material

1st we need to grow the BTO and STO nanomembrane. We grew a water soluble sacrificial layer of $\text{Sr}_3\text{Al}_2\text{O}_6$ (SAO) with a thickness of 30 nm. Next, BTO and STO were grown on top of the SAO using pulsed laser deposition (PLD) with a laser power of 248 nm (KrF gas) and had a thickness of ≈ 10 nm. We then needed to make the nanomembrane freestanding. To do so we deposited a Ni layer through an electron-beam evaporator (E-beam) and sputtering in physical vapor deposition (PVD). The resulting thickness of the Ni is $\approx 2\mu\text{m}$.

II.2. Etching & Transfer

The material was then inserted into water to etch the SAO soluble layer. Overtime we did two types of methods from here out. One of which was where we placed the Ni side of the material onto the Au bottom electrode with the BTO or

STO side facing up. We then put Ag paste onto the top of it to be our top electrode. It was then placed onto a hotplate to remove any excess liquid and help material adhere. This is the transfer process depicted in figure 2 (2). The second method involved transfer the Ni/STO or BTO with the Ni side up on the Au electrode. We then etched the Ni by using a FeCl_3 solution and added Ag paste to act as the top electrode. It was then also placed onto a hotplate.

III. MEASUREMENTS

III.1. First Samples & Tests

After the preparing the samples, we hooked them up to a multimeter. With the probes on the top and bottom electrode to measure the current and voltage across the device. This was done to see if we could observe the typical hysteresis loop that a memristor exhibits. We also wanted to measure the impedance and conductivity of the device to see if the perovskite material could perform up to the standard metal oxides that are common. Among the first devices created were: TiO_2 , Polycrystalline STO, Singlecrystalline STO, & Singlecrystalline BTO. Crystallinity confirmed using an optical microscope located in the lab. Impedance, Conductivity, & IV curve were measured and can be found in figure 3 (3). The memory performance of our perovskite materials didn't perform very well as can be seen. The single BTO sample was ferroelectric & the memory performance was not stable and barely visible. The Poly STO didn't have any memory performance visible and displayed a fairly linear/ohmic IV curve. Whereas the single STO displayed memory performance but it was very weak. The TiO_2 displayed the strongest of the starting materials by displaying strong impedance and memory performance in the IV curve. However, this would be the first and only time we worked with TiO_2 , as we would fully focus on perovskite materials after this. Based off these findings, our future goals were to 1) improve the stability of BTO and 2) boost the memory performance of STO. To do this, we wanted to look at what other papers findings were and compare their baseline to our work. So, we looked at several papers in ferroelectric memristors and perovskite materials to look at research trends. We looks at the following data in each: device structure, material, electrode, crystallinity, On current or set voltage, off current or reset voltage, on/off ratio, endurance, ion conductivity, and ion resistivity. The full research trend that we came up with can be found in supporting information.

III.2. Second Samples & Tests

We achieved better results by making our samples thinner. We also needed a better multimeter as ours wasn't working well on our experiments. We got to use a much better multimeter system in Dr. Chuan Wang's lab. With that, we measured our samples. This time only the IV curve and set the voltage to go from -1 to 1 V. Two samples stuck out: a single-crystalline STO sample (≈ 10 nm) and a single-crystalline BTO (≈ 10 nm). Crystallinity confirmed using an optical microscope and pictures can be seen in supporting information. The samples measured did not perform well

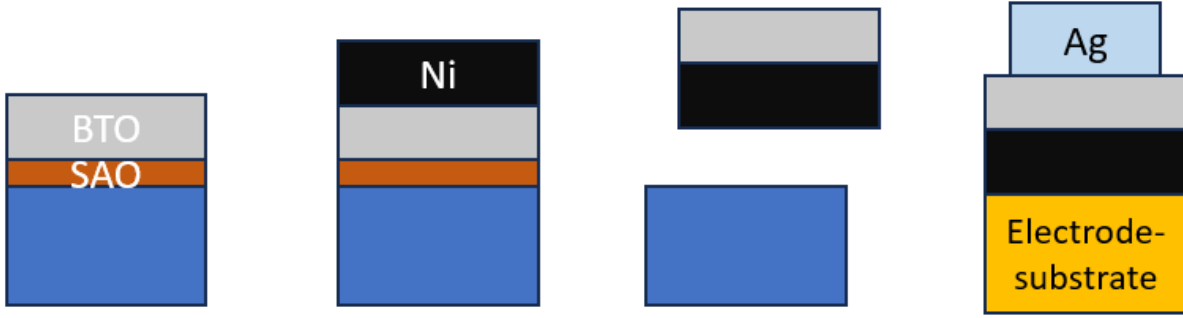


FIG. 2. Nickel deposition on SAO/BTO and transfer to Au electrode with Ag top electrode.

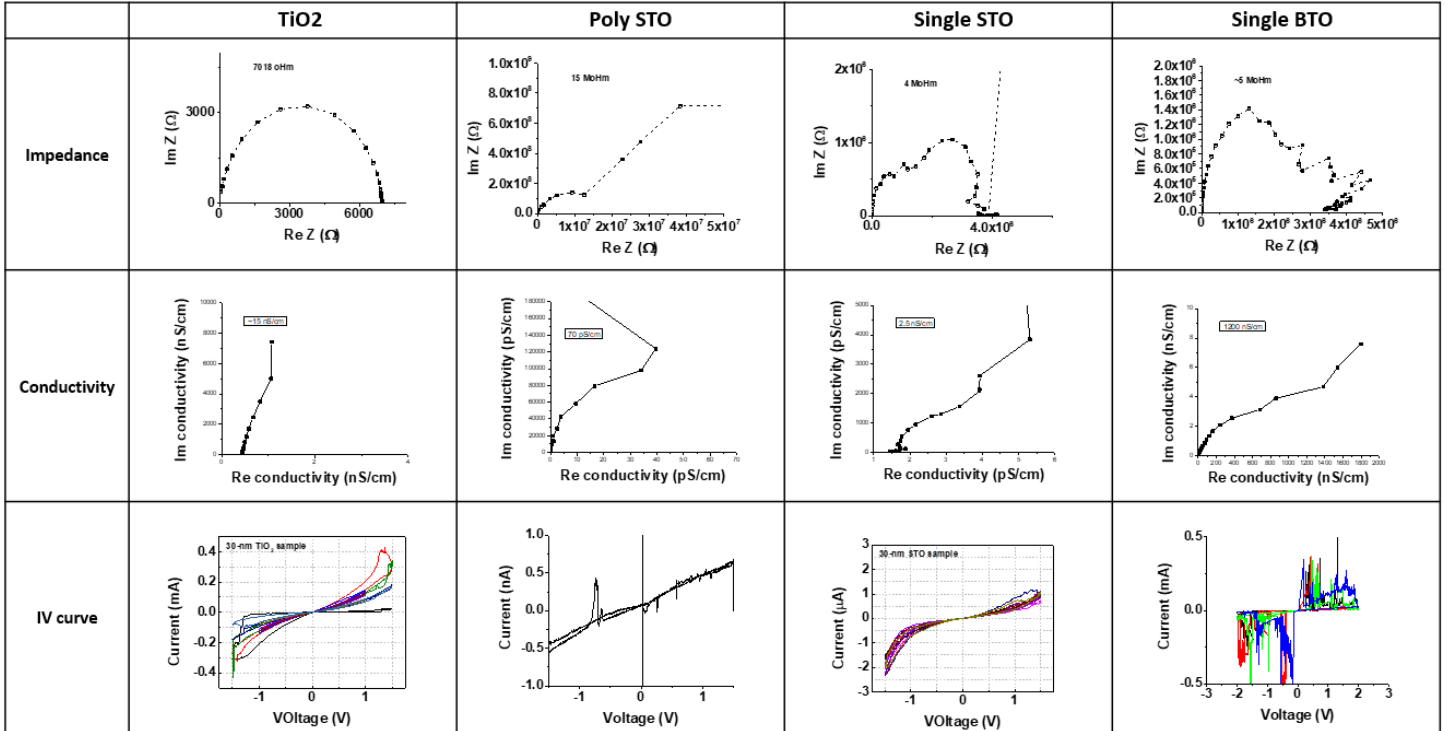


FIG. 3. Impedance, Conductivity, & IV Curve graphs for shown materials.

however. STO displayed better endurance but still poor performance, and failed to reach the on/off ratio that BTO had. However BTO shorted after a while and thus its endurance was fairly low. We measured a poly-crystalline BTO sample (≈ 50 nm) as well and it eventually shorted and didn't display the memory performance very well. There was a large off current that caused poor performance in our materials. We need to increase our on/off ratio to the standard of about 10^3 or 10^4 . We plotted the IV curves in log-scale for clarity and observing behavior. These can be found below (4).

IV. CONCLUSION & FUTURE PROSPECTS

Our results have led us to the deduction that single crystalline is best for our purposes of a memristor that is applicable for future computing properties. Poly-crystalline ma-

terial seems to not be as useful as single-crystalline. This is likely because of poly-crystalline lacking uniformity like single-crystalline and their grain boundary defects acting as a barrier by increasing resistance. With this being said, our best perovskite material is likely single-crystalline STO. It had more consistency due to the fact that it wouldn't short. However our material still wasn't very good compared to the standard of memristors being researched. We need to learn more about our material parameters to better evaluate it. Learning about its power consumption, on/off ratio, multi-state resistances, and its linearity. We need to study these parameters more to further improve perovskite memristors, our main goal being to increase its on/off ratio and durability.

One of the main ways we can further improve our device is to lower the number of defects within it and realize a cross-bar structure for the memristor. The defects can be low-

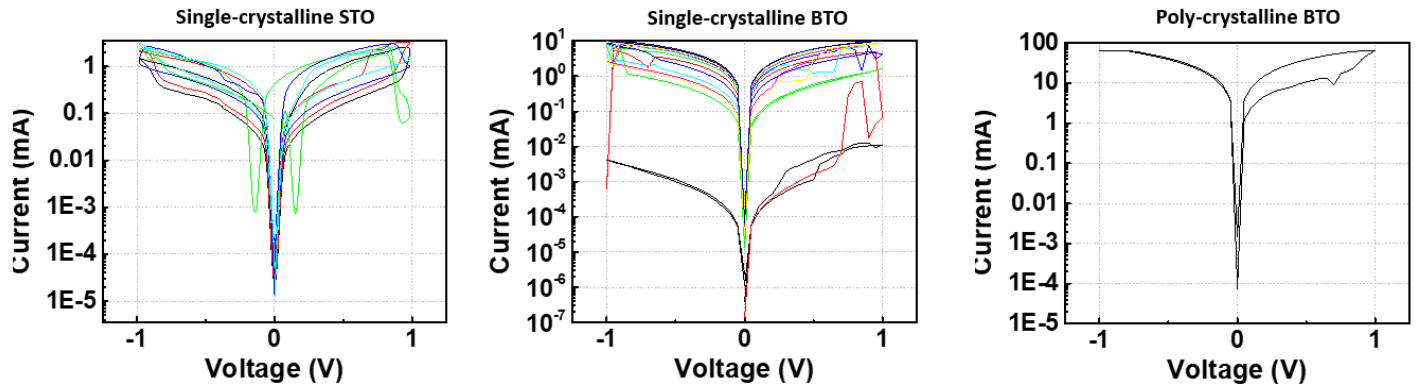


FIG. 4. Log-scale IV curves of single-crystalline STO, single-crystalline BTO, and poly-crystalline BTO.

ered in several ways including: controlling the growth conditions, optimizing the growth techniques (further improving the method the PLD was used to grow our material), annealing our material after growth to better control defects and crystallinity, and doping. We could also characterize what might be wrong and what types of defects we're dealing with by using some method to analyze the material (x-ray diffraction, etc.). The crossbar structure could further improve our device by allowing for a higher memory density to be used in our device. There will be a much higher variation of resistance states that will further allow for better memory applications.

Perovskite materials are promising in the future of memristor technology. They provide a switchable resistance that is crucial for creating a memristor, non-volatile memory, and high density potential for memory devices. Their potential for electronic applications and in-memory computing are what make them enticing. Dr. Bae's group will continue to work with memristor devices to see if more prospective devices can be created.

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